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(54) ELECTRICALLY CONDUCTIVE HOSE

(71) We, SAMUEL MOORE AND COMPANY, a Company organised and existing under the laws of the State of Ohio, United States of America, of 1199, South Chillicothe Road, Aurora, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates generally to composite reinforced hose which is electrically conductive and more particularly to a hose for transmitting a fluid under pressure in a spraying apparatus, for example paint spraying apparatus.

Apparatus for spraying liquids such as paint is provided with a pump and hose assembly for transmitting liquid under pressure from a supply tank to a spray gun nozzle. An electrically conductive ground wire is usually included throughout the length of the hose to drain off any static electricity developed at the spray nozzle of the hose to prevent sparking when it approaches a conductor such as a steel beam. A hose having a flexible polymeric core tube, fibrous reinforcing material wound about the core tube and a protective sheath is used to convey the liquid at a pressure which is sufficiently high to produce a spray. The hose must be capable of expanding radially under the pulsation of the pump in order to act as an accumulator which attenuates the pulses so as to minimize pulsating at the nozzle and thereby produce a relatively smooth and uniform spray of liquid. On electric motor operated paint spray systems, the accumulator action also retards the rate of pressure change affecting the motor controlling pressure switch, thereby reducing the number of stops and starts of the motor controlling the fluid pump.

It has been proposed heretofore to wind a ground wire about the core tube as one of the braids of the reinforcing layer. However, the wire frequently broke under pressure and the abrasion of the braid by the wire sometimes resulted in bursting of the hose.

It is proposed in U.S. Patent Specifications 3,445,583, 3,543,803 and 3,780,208 to provide hoses for transmitting liquids from a pulsating source with a grounding wire helically wound about the core tube and enclosed within a rupture resistant sleeve.

While the disclosed hoses have been found to be adapted for successfully transmitting paints under most conditions, the inclusion of a grounding wire enclosed in a plastics sleeve introduces additional steps in the manufacture of the hose and it has been found in practice that the ground wire sometimes ruptures and the fragments are not confined sufficiently to maintain continuity of the static discharge system. Also, the fragments may pentrate the core or sheath causing a premature failure of the hose.

It is therefore an object of this invention to provide an improved composite hose having a means for static discharge. Another object of the invention is to provide a composite hose for conveying fluids under pressure, such as used with a paint spraying apparatus adapter for transmission of pulsating fluids, and has a static discharge means which is conveniently incorporated in the hose and effectively discharges static electricity throughout the life of the hose. A further object of the invention is to provide a composite hose with a grounding means coextensive with the length of the hose which is not ruptured or otherwise broken by the pulsating action of the hose.

According to the present invention, there is provided a composite reinforced hose for conveying fluids under pressure, which hose comprises a core tube; a fibrous reinforcing material about said core tube; and a protective sheath over the fibrous material; wherein said core tube has an innermost substantially electrically non-conductive synthetic polymer layer, and a synthetic polymer layer rendered electrically conductive by loading with electrically conductive particles, said conductive layer being the

sole means in said hose for conducting electrical current. Although the laminated core tube may be formed by spraying the inner layer with a conductive coating or by dipping the inner layer in a conductive resin, the core tube is preferably formed by coaxially extruding two different extrudable synthetic polymers to provide a flexible tube having a wall of two synthetic polymeric resinous layers. The two layers may be extruded in two separate extrusion steps or they may be simultaneously coextruded so that the layers are melt fused together. The conductive layer extends throughout the entire length of the hose and may be in electrical contact with a grounded hose fitting. The conductive layer is a synthetic polymer which may exhibit a volume resistivity of 10^9 ohm-cm or less.

In airless paint spraying processes, it is undesirable to accumulate more than 1400 static volts at the spray gun of the spraying apparatus because of the danger of igniting the air-solvent mixture about the spray gun. Preferably, a safety factor of 4:1 should be maintained which means that the static voltage on the spray end of the hose should not exceed 350 volts. The hose provided by this invention has a ground which is a conductive layer of polymer which will drain off the static potential so a frightening or dangerous electrical-arc between the spray gun and ground is avoided.

Any suitable conductive synthetic polymer may be used. Preferably, the conductive synthetic polymer is one which will melt fuse to the polymer of the first layer when the two polymers are coaxially extruded. The conductive polymer must have the required electrical properties. While a conductive polymer having a volume resistivity after application and other processing of as high as 100,000 ohm-cm at ambient temperature may be used, usually the volume resistivity will not be more than substantially 2000 ohm-cm. It is preferred to use one having a calculated volume resistivity of not more than about 500 ohm-cm. In fact, best results have been obtained so far with a polymer having a volume resistivity of 40 or less ohm-cm. The volume resistivity may be calculated by the method described in "NFPA Journal No. 77, Static Electricity, 1972." Examples of suitable polymers are ethylene-ethyl acrylate, ethylene-vinyl acrylate and thermoplastic rubber having the desired volume resistivity but it is preferred to use a polyurethane of the desired volume resistivity in hoses having a nylon inner layer where kink resistance is desirable because the polyurethane bonds well to the nylon and can be bonded to the reinforcing material.

The conductive polymer may have carbon particles including graphite particles, silver particles, copper particles or other suitable electrically conductive particles dispersed substantially uniform therein to provide the polymer with a volume resistivity within the requirements of the hose.

The invention permits the manufacture of a composite reinforced conductive paint hose having some particularly desirable physical property without substantial compromise of other desirable properties combined with a means for effectively draining static electricity from the hose. For example, a substantially chemically resistant polymer such as nylon may be chosen for the inside layer of the core tube wall and a layer of a more flexible polymer such as an elastomeric polyurethane having electrically conductive particles dispersed therein may be fused thereto as the outer surface to provide improved flexibility, kink resistance and means for preventing sparking of static electricity at the nozzle of the hose. The outer layer containing electrically conductive particles may be shaped from a resin such as a polyurethane which can be solvated with a polar solvent to adhesively bond the core tube to the adjacent layer of reinforcing material and to improve the strength of the hose. In such a hose, the relative thickness of the nylon and conductive polyurethane layers may be varied to further modify the properties of the hose.

The core tube may be fabricated by any suitable simultaneous coaxial extrusion process which will produce melt fusion of two different layers of synthetic thermoplastics polymeric resins together to the extent that the two layers will not separate at the interface under elongation and other conditions to which the hose will be exposed. The most practical method of making the core tube is to supply two different synthetic thermoplastics polymeric resins or two different types of the same synthetic thermoplastics polymeric resin to a single extrusion head from different extruders operating under conditions whereby the resin which will be the inner portion of the core tube is still molten when the molten resin for the other portion of the core tube wall is applied thereover and the two molten synthetic resins are extruded through the same extrusion die.

It has been found that two layers of selected thermoplastics synthetic polymeric resin with one being electrically conductive will melt fuse together along the interface and become so firmly bonded together that the core tube will not delaminate in a hose used to convey fluids under high pressure even if the physical properties of the two layers are significantly different. For example, nylon and a conductive thermoplastic polyurethane having particles of carbon black uniformly dispersed therein

will melt fuse together in accordance with the process of the invention. Hence, the invention contemplates a conductive paint hose having a core tube with a layer of nylon melt fused to a layer of thermoplastic substantially non-porous polyurethane. The innermost layer may be nylon because of its chemical resistance. The conductive polyurethane layer imparts flexibility to the hose and may also be used for making an adhesive to bond the core tube to the fibrous reinforcing layer so it is usually disposed on the outside of the core tube.

The invention may also provide composite reinforced hoses having a core tube of two or more layers of synthetic polymeric resin of the same general chemical composition but modified to provide different physical properties. For example, a relatively hard thermoplastic polyurethane having a hardness of Shore D 50 to 60 and a relatively soft thermoplastic polyurethane having a hardness of Shore A 80 to 95 may be co-extruded to form a core tube. The harder thermoplastic polyurethane has better chemical resistance than the softer one so the harder one is usually the innermost layer of the core tube while the softer one contains particles of an electrical conductor and is the outer layer. The presence of the layer of softer polyurethane improves the flexibility of the hose as well as providing a conductor for static electricity.

Other combinations of synthetic polymeric resins which may be co-axially extruded simultaneously or in tandem to form a core tube having two or more layers have been proposed. For example, segmented co-polyesters such as "Hytrel" (Registered Trade Mark) as the insulating layer and a polyvinyl chloride compound for the conductive layer. A segmented co-polyester may be used for the insulating layer and a conductive substantially non-porous thermoplastic polyurethane as the conductive layer. A mechanical mixture of an aromatic polyester such as poly(tetramethylene terephthalate) and a segmented co-polyester may be used as the insulating layer and a conductive polyvinyl chloride polymer as the outer layer. The laminated core tubes combining a layer of "Hytrel" (Registered Trade Mark) or a mixture of a segmented co-polyester and an aromatic polyester and a layer of polyvinyl chloride compound or polyurethane will have the layer containing the segmented co-polyester on the inside as the non-conductive layer. A mechanical mixture of segmented co-polyester and polyurethane may also be used for one of the layers, usually the outer layer. The inner layer of the core tube may be a mixture containing from 5 to 95% by weight polyurethane and 95 to 5% by weight aromatic polyester in combination with any of the outer layers disclosed herein. The inner layer may also be a mixture of polyacetal and polyurethane in combination with any of the outer layers. In these embodiments, the outer layer contains particles which are electrically conductive.

Examples of suitable thermoplastic aromatic polyesters are "Valox" (Registered Trade Mark), aromatic polyester sold by the General Electric Co., "Tenite" (Registered Trade Mark), aromatic polyester sold by Eastman Kodak Co. and "Celanex" (Registered Trade Mark), aromatic polyester sold by Celenese Plastics Co.

Any suitable relative proportions of aromatic polyester such as "Valox" (Registered Trade Mark) and segmented co-polyester such as "Hytrel" (Registered Trade Mark) may be used in the mixtures thereof extruded to form a layer of the core tube. For example, from 5% to 60% by weight aromatic polyester and 95% to 40% by weight segmented co-polyester may be used. Any suitable mixture of polyurethane and co-segmented polyester may be used, but it is preferred to use from 99 to 50% thermoplastic polyurethane and 1% to 50% by weight co-segmented polyester.

Best results have been obtained so far with a hose having a core tube with an inner nylon surface and a conductive polyurethane surface so such a core tube is preferred. However, other polymers which are resistant to chemical action by that paint may be used for the inner layer such as a segmented co-polyester such as "Hytrel" (Registered Trade Mark) sold by E.I. duPont de Nemours of Wilming ton, Delaware.

The core tube may be adhesively bonded to the surface of the reinforcing material by the application of an adhesive material or by activating the surface of the core tube with a solvating or softening agent to form an adhesive *in situ* from the resin on the other surface of the core tube. For example, a polyurethane surface of a core tube may be activated by wetting it with a suitable polar solvent such as, for example, N-methyl pyrrolidone. However, it is preferred to apply an adhesive material such as a solution of polyurethane between the surface of the core tube and an adjacent layer of fibrous reinforcing material because the use of a solvating agent to solvate the surface disturbs the uniformity of the distribution of electrically conductive particles and affects the electrical conductivity of the semi-conductive polymer layer. The reinforcing fibrous material may be then applied under tension about the adhesively wet core tube whereby the strands of reinforcing material become embedded and partially encapsulated by the adhesive. In this way, the fibrous reinforcing layer be-

comes bonded to the core tube and the strength of the hose is improved.

It has been found that simultaneously co-extruded properly selected synthetic thermoplastic polymers will become bonded together by melt fusion even though one of the polymers contains particles of electrically conductive material and that an intermediate adhesive is not necessary. For example, nylon will fuse to a thermoplastic elastomeric polyurethane containing carbon black particles if the top molten synthetic polymers are fed separately to an extrusion head and coextruded one over the other while still molten. In those instances where one layer of the core tube is difficult to melt fuse to another layer, an intermediate layer of a third synthetic resin which will melt fuse to both layers may be interposed therebetween but it is preferred to melt fuse the conductive layer directly to the inner layer of the core tube.

The invention will now be described by way of example to the accompanying drawin which:—

Figure 1 is a cut-away side elevation, partially in section, of one embodiment of the invention; and,

Figure 2 is a cross section, on an enlarged scale, on the line 2—2 of Fig. 1.

Referring now to the drawing, a conductive paint hose 10 having a core tube I.D. of 0.25 inch is illustrated in Figures 1 and 2. Composite hose 10 is formed of a cylindrical inner or core tube 17 formed by the simultaneous coaxial extrusion of an electrically non-conductive layer of nylon 11 substantially 0.025 inch thick which has an electrically conductive thermoplastic elastomeric polyurethane radially outer layer 12 substantially 0.015 inch thick; the outer layer 12 contains carbon particles and has a volume resistivity at room temperature substantially (20°C.) of substantially 100 ohm-cm. The two synthetic polymeric resins become fused together at the interface to form the core tube 17 which will not delaminate when the hose 10 is used for conveying a paint under pulsating pressure. The radially outer surface of polyurethane of core tube 17 is wet with an adhesive solution 13 of a polyurethane in N-methyl pyrrolidone. A first reinforcing layer 14 of nylon filaments is braided under tension around the core tube while the adhesive on the surface of core tube 17 is wet. The filaments become bonded to the surface of the core tube 17 forming an elastomeric bond of the fibrous reinforcing material with the core tube. A second reinforcing layer 15, which is formed of poly(ethylene terephthalate)ester, is braided over layer 14. A protective polyurethane sheath 16 substantially 0.025 inch thick is extruded over fibrous reinforcing layer 15 by extrusion of a thermoplastic elastomeric polyurethane thereover. Sheath 16 may be adhesively bonded to the surface of layer 15.

Any other core tube similar to those disclosed as suitable herein may be substituted in the foregoing embodiment of the invention for the core tube 17, and the core tube 17 may or may not be bonded to the first reinforcing layer depending upon the particular requirements of the hose.

The polyurethane layer 12 of core tube 17 may be extruded from any suitable thermoplastic polyurethane such as the one sold under the trademark "Pellethane" (Registered Trade Mark) by the Upjohn Company. The polyurethane disclosed in U.S. Patent Specifications 3,116,760 and 3,722,550 and disclosed in the book by Saunders and Frisch, entitled *"Polyurethanes: Chemistry and Technology"*, published by Interscience Publishers, copyright 1964 may also be used. Reaction products of poly(tetramethylene ether)glycol, suitable chain extender such as 1,4 butane diol, and 4,4'-diphenylmethane diisocyanate and polyurethanes prepared by reacting an inner ester such as poly(e-caprolactone)ester and a suitable chain extender such as 1,4 butane diol with an aromatic diisocyanate such as 4,4'diphenylmethane diisocyanate are preferred. The sheath 16 may also be extruded from any other suitable synthetic resin such as, for example, nylon.

The fibrous reinforcing material may be formed by braiding filaments or by helically winding strands of filaments of any suitable synthetic resinous material, such as, for example, a poly(alkylene terephthalate)ester, nylon, aromatic polyamide or combinations thereof. Suitable nylon fibrous reinforcing material is disclosed in U.S. Patent Specification 3,334,164 while suitable poly-(alkylene terephthalate)ester fibrous reinforcing material is disclosed in U.S. Patent Specication 3,062,241. Such fibers have a tenacity of 7 to 11 grams per denier and an elongation at break of 9% to 17%. In one embodiment of the invention, the hose may be provided with a reinforcing layer of braided or helically wound filaments having a tenacity of at least 13 grams per denier and up to substantially 25 grams per denier and an elongation at break of from 2% to 7% such as the aromatic polyamide fibre marketed by E.I. duPont de Nemours & Co. under the trademark "Kevlar" (Registered Trade Mark). Suitable reinforcing material containing synthetic aromatic polyamide filaments is disclosed in U.S. Patent Specification No. 3,905,398 issued September 16, 1975. A fibrous reinforcing material of aromatic polyamide fibers may be used to advantage in composite hoses having a high burst strength.

The core tube can be shaped by extrusion

with any suitable extrusion apparatus having a separate extruder for feeding each synthetic thermoplastic polymeric resin to a single extrusion head.

WHAT WE CLAIM IS:—

1. A composite reinforced hose for conveying fluids under pressure, which hose comprises a core tube; a fibrous reinforcing material about said core tube; and a protective sheath over the fibrous material; wherein said core tube has an innermost substantially electrically non-conductive synthetic polymer layer, and a synthetic polymer layer rendered electrically conductive by loading with electrically conductive particles, said conductive layer being the sole means in said hose for conducting electrical current.

2. A hose as claimed in Claim 1 wherein said core tube layers are melt fused together.

3. A hose as claimed in Claim 1 or Claim 2, wherein said innermost layer of said core tube is nylon, and said electrically conductive layer fused thereto is a polyurethane.

4. A hose as claimed in any one of the preceding claims wherein electrically conductive layer contains carbon particles.

5. A hose as claimed in any one of the preceding claims wherein said electrically conductive layer is polyurethane having a volume resistivity of not more than substantially 2000 ohm-cm.

6. A hose as claimed in Claim 1 or Claim 2 wherein said electrically conductive layer of the core tube has particles of electroconductive material distributed therein and a volume resistivity of not more than substantially 2000 ohm-cm.

7. A hose of Claim 2 wherein said core tube has only two layers, and said innermost layer is nylon and the outer layer is polyurethane having carbon particles distributed therein, said outer layer being bonded to the fibrous reinforcing material.

8. A hose as claimed in any one of the preceding claims wherein the fibrous reinforcing material is nylon, poly (alkylene terephthalate) ester or an aromatic polyamide.

9. A hose as claimed in any one of the preceding claims wherein said sheath is a thermoplastic polyurethane.

10. A hose as claimed in any one of the preceding claims wherein said sheath is bonded to said fibrous reinforcing material.

11. A hose as claimed in Claim 1 or Claim 2 wherein said core tube is (1) a core tube comprising an inner layer of segmented co-polyester and an outer layer of polyvinyl chloride compound, or (2) a core tube having an inner layer of a mixture of segmented co-polyester and a thermoplastic aromatic polyester and an outer layer of polyvinyl chloride compound, segmented co-polyester, polyurethane or a mixture of segmented co-polyester and polyurethane, or (3) a core tube having an inner layer of a mixture of polyurethane and a segmented co-polyester and an outer polyurethane layer, or (4) a core tube having an inner layer of a mixture of a thermoplastic aromatic polyester and polyurethane and an outer layer of polyvinyl chloride compound, segmented co-polyester, polyurethane or a mixture of segmented co-polyester and polyurethane, or (5) a core tube having an inner layer of a mixture of polyacetal and polyurethane and an outer layer of polyvinyl chloride compound, segmented co-polyester, polyurethane or a mixture of segmented co-polyester and polyurethane and said outer layer contains electrically conductive particles.

12. A composite reinforced hose substantially as herein described with reference to, and as illustrated in, Figures 1 and 2 of the accompanying drawings.

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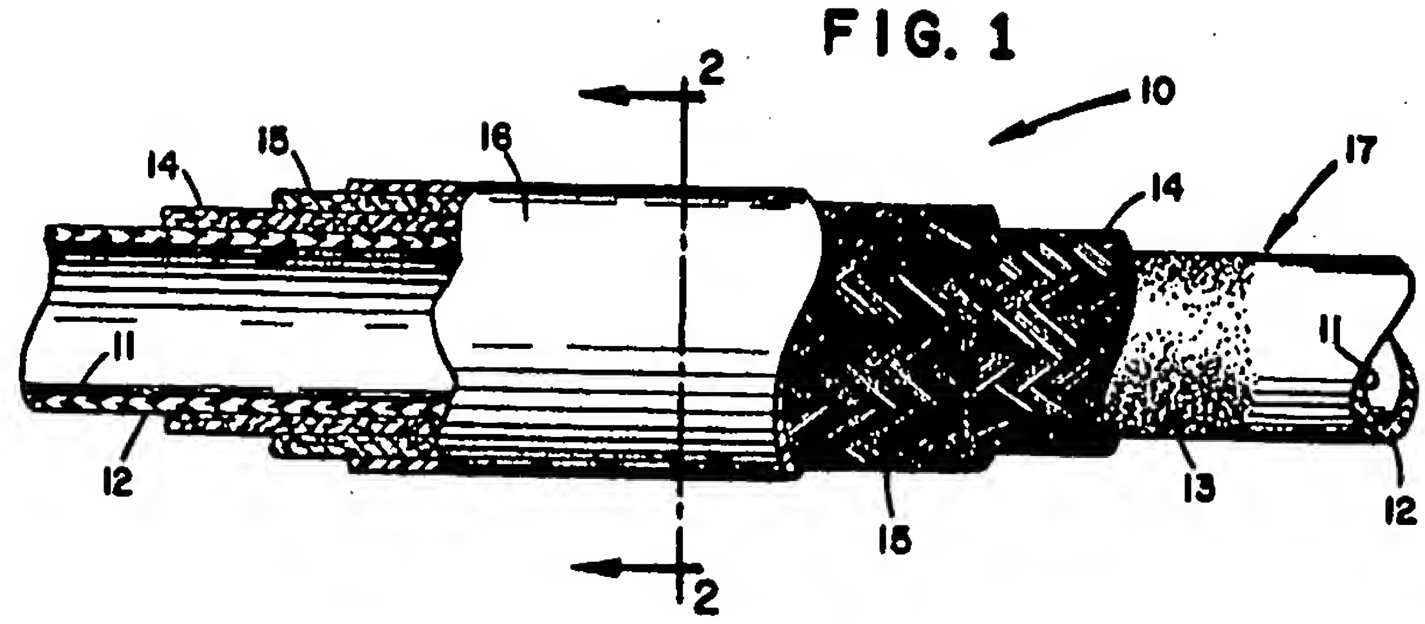
1562435 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

FIG. 1



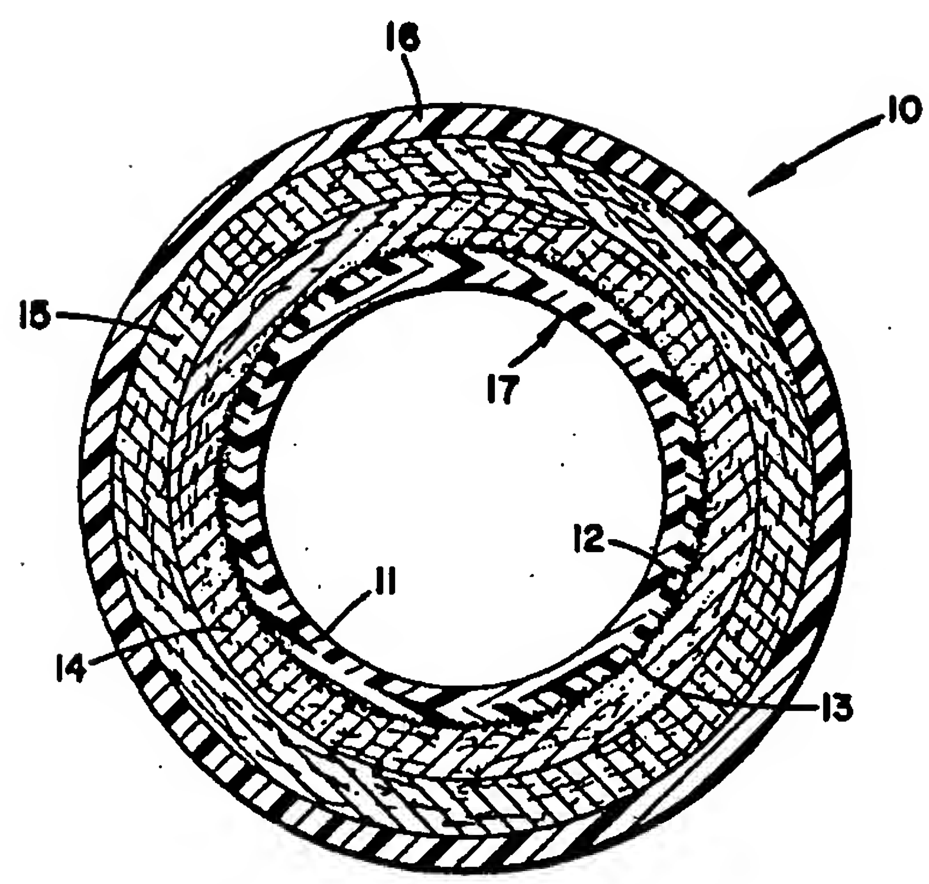


FIG. 2

EP1054036

Publication Title:

Reinforced polymers

Abstract:

Provided is a method for the production of a reinforced polymer, which method comprises: (a) introducing carbon nanotubes into a polymer to provide a mixture of the polymer and the nanotubes; (b) stretching the mixture at or above the melting temperature (Tm) of the polymer; and (c) stretching the mixture in the solid state so as to orient the carbon nanotubes.